

WET ETCH PROCESS AND COMPOSITION FOR FORMING
OPENINGS IN A POLYMER SUBSTRATE

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] The present application claims the benefit of United States Provisional Application No. 60/222,362, filed August 1, 2000, the disclosure of which is hereby incorporated by reference herein.

BACKGROUND OF THE INVENTION

[0002] The present invention relates in general to the field of microelectronic elements, and more particularly, to chemical processes and compositions therefore for forming openings such as windows, vias and/or through holes in polymer substrates. Still more particularly, the present invention relates to etch compositions providing a color signal indicator at the completion of the etch process.

[0003] Windows, vias and other openings are common features incorporated in microelectronic elements enabling the interconnection of microelectronic components and circuit features on opposing sides of a substrate, typically, a dielectric substrate such as a flexible sheet of polyimide. Micro-vias, i.e., those having a diameter of less than about 100 microns, play an important role in high I/O density IC packages. There are known a number of techniques for making vias and/or other openings in polymer substrates. These techniques include laser ablation, photo imaging/plasma etching and chemical etching, of which chemical etching has generally been preferred. In this regard, laser ablation often leaves a residue which requires a subsequent plasma cleaning step to remove the residue to enable the subsequent metalization process to be performed. This two-step laser ablation process is not only time consuming, but also

increases manufacturing costs. In addition, laser ablation generally can only process one substrate at a time.

[0004] Chemical etching, on the other hand, has a number of advantages which cannot be obtained by laser ablation. For example, substrates can be processed by either rack or batch processing for high production rates. Chemical etching has been found to provide clean and even vias, providing a low cost and simple process with inherent workability. In this regard, chemical etching is suitable not only as an alternative process for forming vias, but also for reworking of vias formed by laser ablation and/or plasma etching techniques which have been incompletely formed.

[0005] There are known various etching solutions suitable for forming vias and/or openings in flexible dielectric substrates such as polyimide. For a variety of reasons, these known etching solutions suffer a number of disadvantages wherein improvements in chemical etching techniques have been sought. For example, alcohol-based etchants, such as ethanol or isopropanol solutions as disclosed in U.S. Patent No. 4,986,880 are highly volatile and evaporate quickly, i.e., boiling point of about 160°F. These alcohol-based etchants are hard to control due to rapid depletion of the active components.

[0006] Aqueous etching solutions such as known from U.S. Patent Nos. 5,350,487, 4,911,786, 4,857,143 and 4,353,778 are effective in removing the polyimide material, but often cause contact pad blisters when used in forming vias in two metal polyimide structures, i.e., a polyimide substrate clad on its opposing surfaces with a copper layer, or when used with one metal polyimide structures. Another problem with using aqueous etching solutions in single metal polyimide structures is that a mask, a resist or another protect layer must be used to protect the surface of the polyimide which is not metal clad.

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[0007] Solvent-based etchants, such as TMAH-based as known from U.S. Patent Nos. 4,369,090, 4,039,371, 5,597,983 and 5,653,893, hydrazinehydrate-based such as known from U.S. Patent No. 4,436,583 and JP 3101228A2, and hydroxylamine-based such as known from U.S. Patent No. 5,279,771 are known to attack adhesives that are commonly employed in framing processes used to stabilize the polyimide substrate such as disclosed in U.S. Patent Application No. 09/134,212 entitled "Dicing in Registration With Solder Balls", filed on August 14, 1998 and assigned to the same assignee of the present application. Solvent-based etchants are therefore undesirable due to the tendency to separate the copper clad polyimide material from the glass frame. In addition, these solvent-based etchants will have the tendency to cause the copper contact pads to form blisters by delamination of the contact pads from the polyimide substrate.

[0008] Accordingly, it can be appreciated that there is the need for further improvements in chemical etchants which avoid the above disadvantages, while being low cost, incorporating simple process techniques and providing for reworkability of vias and openings formed by other techniques such as laser ablation and/or plasma etch processes. Still further, there is the desirability of providing a chemical etchant which provides a color indicator which signals completion of the etching process. This ensures complete etching of the polymer substrate thereby minimizing operator error and the degree of reworking required in forming vias and other openings.

SUMMARY OF THE INVENTION

[0009] In accordance with the present invention there is provided a chemical etch composition for forming openings in polymer substrates, in particular, micro-vias having a diameter of about 100 microns or less. The etchant compositions of the present invention further provide a color indicator which signals completion of the etching process,

e.g., the appearance of a red color at the base of the opening being etched.

[0010] The present invention discloses glycol-based etchant compositions for etching openings, in particular, micro-vias, in polymer substrates. These etchant compositions have higher boiling points, by way of example, of preferably about 240°F to 300°F, more preferably of about 260°F to 280°F, and hence, are not highly volatile. The etchant compositions of the present invention are more stable than alcohol-based formulations, making them easier to control. In addition, glycol-based etchant compositions are less likely to attack the adhesive that are typically used in microelectronic elements and/or in bonding metal clad polyimide material to a glass frame. The method and etchant compositions of the present invention produce clean and even vias or openings in a two-step process, i.e., (1) dipping the substrate in the etchant composition, preferably until a red signal color covers the via opening and (2) rinsing with pressurized water, i.e., about 30 psi, until the red color when present disappears from the via.

[0011] In accordance with one embodiment of the present invention there is described a composition for etching a polymer substrate comprising a dihydric alcohol having from two to five carbon atoms, a hydroxide compound selected from the group consisting of lithium hydroxide, sodium hydroxide, potassium hydroxide, calcium hydroxide, barium hydroxide, strontium hydroxide and mixtures thereof, and water.

[0012] In accordance with one embodiment of the present invention there is described a composition for etching a polymer substrate comprising glycol, potassium hydroxide and deionized water, wherein the glycol and the water are present in a ratio of from about 0.5:1 to about 8.5:1 and the potassium hydroxide is present in an amount of from about 40 to about 80 grams per 100 ml of glycol and water solution.

in accordance with the present invention which is used as a tented stencil for printing a material, such as flux or solder paste, onto the top surface of a solder ball; and

[0018] Fig. 5 is a perspective diagrammatic illustration of a tented stencil made in accordance with the present invention.

DETAILED DESCRIPTION

[0019] In describing the preferred embodiments of the present invention, specific terminology will be resorted to for the sake of clarity. However, the invention is not intended to be limited to the specific terms so selected, and is to be understood that each specific term includes all technical equivalence which operate in a similar manner to accomplish a similar purpose.

[0020] In accordance with the present invention, there is disclosed a chemical etching process and chemical etchant composition for wet chemical etching of polymer substrates, e.g., polyimide, to form openings such as bond windows, vias and other holes, and particularly, micro-vias, i.e., an opening having a diameter of about 100 microns or less, for interconnecting layers in flexible circuit structures of microelectronic elements. The etching process and etchant compositions are broadly based upon the presence of at least one dihydric alcohol and a strong base such as one or more hydroxide compounds.

[0021] Dihydric alcohols contemplated for use in accordance with the present invention include diols and glycols having a chain length of preferably 2 to 5 carbon atoms, and more preferably from 2 to 4 carbon atoms. In accordance with the preferred embodiment, the etchant composition includes ethylene glycol. Although it is contemplated that dihydric alcohols having a chain length of 5 carbons or greater can be used, it is known that higher molecular weight diols and glycols will result in increased viscosity to the etchant

composition, thereby imparting poor wetting properties. In addition, as the molecular weight of the dihydric alcohol increases, it is contemplated that there may be solubility limitations of the other components, e.g., the hydroxide compound, to form the required composition in the nature of a solution without precipitation of the hydroxide compound.

[0022] Various strong bases such as hydroxide compounds are suitable for use in the etchant composition in accordance with the present invention. For example, suitable hydroxide compounds include lithium hydroxide, sodium hydroxide, potassium hydroxide, calcium hydroxide, strontium hydroxide, barium hydroxide and mixtures thereof. Using weaker hydroxide compounds, although suitable, will result in longer etching times. On the other hand, stronger hydroxide compounds will result in shorter etching times. Although sodium hydroxide can be used, it may have the tendency to cause blisters at the contact pads, as well as being less soluble than other hydroxide compounds such as potassium hydroxide potentially causing precipitation. When etching polyimide substrates, lithium hydroxide, barium hydroxide, strontium hydroxide, sodium hydroxide and potassium hydroxide are preferred. Sodium hydroxide and potassium hydroxide are most preferred. It is further contemplated that mixtures of various hydroxide compounds can also be used, for example, potassium hydroxide, sodium hydroxide and others.

[0023] Broadly by way of example, the etchant compositions in accordance with the present invention include from about 30 to about 100 ml of dihydric alcohol, from about 15 to about 80 grams of a strong hydroxide base, from about 1 to about 20 grams of an optional etch speed inhibitor, and up to about 70 mls of water, preferably deionized water. In the preferred etch composition of the present invention, the dihydric alcohol is a glycol, e.g., ethylene glycol, present from about 50 to about 100 ml, the hydroxide base is potassium hydroxide

from about 40 to about 80 grams, from about 1 to 20 grams of etch inhibitor and from about 15 to 50 mls of deionized water. The etch speed inhibitor can be selected from compounds including NaF, CH₃COONa, CH₃COOK, K₂CO₃, Na₂CO₃, K₃PO₄ and hexamethylene tetramine, as well as mixtures thereof. The etch speed inhibitor allows for additional control of the etch speed during the etching process.

[0024] The etchant compositions are generally prepared by combining the dihydric alcohol and deionized water in a vessel and adding a sufficient quantity of hydroxide base which would form a saturated solution at about 150°F. A quantity of the etch speed inhibitor may optionally be added. As the amount of water increases, the amount of hydroxide base should also be increased to maintain a saturated solution at the selected temperature. If water is lost during the process, or if the temperature during the etching process drops, the hydroxide will generally not precipitate out. In this regard, it is contemplated that the etching process will occur at a temperature higher than the saturation temperature of the etchant composition.

[0025] It has been determined that low concentrations of the base such as potassium hydroxide may not produce the color signal at the end of the etching process. Therefore, it is preferred that higher concentrations of hydroxide base be present in the etch compositions where a color signal is desired. The minimum amount of hydroxide base can be determined experimentally, and preferably, should form at least a 50% solution with the water present in the composition. The mechanism of the formation of a red color signal will be explained by way of contemplated theory, and is not to be interpreted as a limitation on the scope of the present invention. During the etching process, a hydrolysis reaction takes place in which the polyimide is broken down. The reaction products of this hydrolysis reaction can be

referred to as a hydrolyzate. It is contemplated that one of the hydrolyzates has a structure which is similar to the structure of a phenolphthalein. Phenolphthalein is an acid-base indicator used in titration. When using phenolphthalein, a pink color is observed when the pH is 8 and a red color is observed when the pH is about 10. It is contemplated that as the hydrolysis reaction proceeds, a color indicating hydrolyzate is produced but it is not until the etching is complete that concentration of color-indicating hydrolyzate is sufficient to produce an obviously visible red color, and hence, a color signal.

[0026] In accordance with a specific example, an etchant composition is prepared including from about 50 to about 100 ml ethylene glycol, from about 50 to about 40 grams potassium hydroxide, up to about 5 grams potassium carbonate, and up to about 50 mls deionized water. The etchant composition is prepared as previously described for use in etching a polyimide substrate to form micro-vias having openings less than about 100 microns in diameter.

[0027] A test substrate was prepared for etching. As shown in Fig. 1, the substrate 100 includes a polyimide flexible layer 102 and outer metal layers 104, 106. The polyimide layer 102 has a thickness of approximately 50 microns, while the metal layers 104, 106 each have a thickness of about 5 microns. Generally, the metal layers are copper formed in a cladding or other depositing process. However, other metals and composites such as nickel/chrome, tin/gold/chromium and the like can be used in place of, or in addition to, copper.

[0028] One or both of the metal layers 104, 106 can be pre-etched into a desired pattern at the desired via sites to expose the polyimide layer 102 in a predetermined pattern. In the case of single metal substrates for use in making certain types of chip scale and near chip scale packages, such as for example the assemblies disclosed in certain embodiments of

containing deionized water and potassium hydroxide, (b) glycol-based compositions containing ethylene glycol and potassium hydroxide, (c) etchant compositions containing varying amounts of deionized water, ethylene glycol and potassium hydroxide, (d) etchant compositions containing deionized water, ethylene glycol, potassium hydroxide and different etch inhibitors, and (e) specific identified compositions.

[0031] Copper clad/polyimide test substrates 100, as previously described, were soaked in hot deionized water at a temperature of from about 140 to about 180°F for 2 to 3 minutes. The purpose of the soaking was to wet the polyimide and to drive bubbles out of the patterned via areas. The substrates 100 were dipped in the etchant compositions at 200°F followed by post cleaning in hot water at a temperature of from about 140° to about 180°F. The cleaned substrates 100 were spray rinsed with deionized water and dried with an air gun. The specific etchant compositions and observations are shown in the following tables.

a. Water base:

FORMULA	OBSERVATION
Test 1: DI water 100ml; KOH 30g	200° F boiling, pad peel off
Test 2: DI water 100ml; KOH 60g	200° F 3 min.: discolor; 5 min.: pad blister
Test 3: DI water 100ml; KOH 60g; NaCO ₃ 5g	200° F 5 min.: discolor; 8 min.: pad blister
Test 4: DI water 100ml; KOH 100g	200° F 2 min.: red color; 5 min.: pad blister

b. Glycol base:

FORMULA	OBSERVATION
Test 5: Glycol 100ml; KOH 20g	220° to 230° F 15 min. undercut
Test 6: Glycol 100ml; KOH 40g	Hard to be dissolved

c. Ration of water: Glycol

FORMULA	OBSERVATION
Test 7: DI water 100ml; Glycol 20ml; KOH 60g	200° F for 10 minutes, 100% of pad blister
Test 8: DI water 100ml; Glycol 50ml; KOH 60g	200° F for 10 minutes, about 50% blister
Test 9: DI water 100ml; Glycol 50ml; KOH 80g	200° F for 10 minutes, about 20% blister
Test 10: DI water 50ml; Glycol 50ml; KOH 60g	200° F for 10 minutes, blister
Test 11: DI water 50ml; Glycol 50ml; KOH 80g	200° F for 10 minutes, none blister
Test 12: DI water 50ml; Glycol 100ml; KOH 60g	200° F for 10 minutes, none blister
Test 13: DI water 30ml; Glycol 70ml; KOH 60g	200° F for 10 minutes, none blister
Test 14: DI water 20ml; Glycol 80ml; KOH 50g	200° F for 10 minutes, none blister
Test 15: DI water 10ml; Glycol 90ml; KOH 40g	200° F for 10 minutes, none blister

d. Different additive/inhibitor:

FORMULA	OBSERVATION
Test 16: DI water 100ml; Glycol 50ml; KOH 80g; K ₂ CO ₃ 20g	200° F for 10 minutes, blister
Test 17: DI water 100ml; Glycol 50ml; KOH 80g; K ₃ PO ₄ 20g	200° F for 10 minutes, none blister
Test 18: DI water 100ml; Glycol 50ml; KOH 80g; NaF 1.5g	200° F for 10 minutes, blister
Test 19: DI water 100ml; Glycol 50ml; KOH 80g; NaCH ₃ COO 20g	200° F for 10 minutes, none blister
Test 20: DI water 100ml; Glycol 50ml; KOH 80g; K ₃ PO ₄ 10g; Hexamethylene tetramine 0.5g	200° F for 10 minutes, none blister

e. Defined formula:

FORMULA	OBSERVATION
1. Glycol 100ml; DI water 50ml; KOH 80g; Hexamethylene tetramine 1g	200° F for 4 min., red color; 6 min. discolor; 7 min. finished, none blister
2. Glycol 100ml; DI water 50ml; KOH 50g; K3PO4 20g	200° F for 5 min., red color; 7 min. finished, none blister
3. Glycol 100ml; DI water 50ml; KOH 80g; K3PO4 1.5g	200° F for 3 min., red; 4 min. discolor; 5 to 6 min. finished, none blister
4. Glycol 80ml; DI water 20ml; KOH 50g; Hexamethylene tetramine 1g	200° F for 4 min., red color; 8 to 10 min. finished, none blister
5. Glycol 80ml; DI water 20ml; KOH 60g; K3PO4 5g	200° F for 6 min., red color; 8 to 10 min. finished, none blister
6. Glycol 85ml; DI water 15ml; KOH 40ml	220° F for 6 min., red color; 8 to 10 min. finished, none blister
7. Glycol 50ml; DI water 50ml; KOH 75g; K3PO4 10g	200° F for 4 min., red color; 6 to 7 min. finished, none blister
8. Glycol 50ml; DI water 50ml; KOH 80g; Hexamethylene tetramine 1g	200° F for 3 min., red color; 4 min. discolor; 5 to 6 min. finished, none blister
9. Glycol 50ml; DI water 50ml; KOH 80g; K3PO4 1.5g	200° F for 3 min., red color; 4 min. discolor; 5 to 6 min. finished, none blister

[0032] The test data evidences that etching substrate 100 based on the use of potassium hydroxide can effectively remove polyimide material in forming vias. Of particular interest are forming micro-vias having a diameter of about 100 microns or less. In the formation of micro-vias, it is desirable that (1) any residual polyimide along the sidewalls be completely removed, and (2) the copper layer, in particular the copper pads around the via openings should not be damaged by the etchant such as by blistering or otherwise. To achieve these objectives, proper etching speed and degree should be maintained during the etching process. It is contemplated

that proper etching speed and degree is dependent upon a number of factors, including the ratio of dihydric alcohol to water, the concentration of the hydroxide component, the inclusion of an etch speed inhibitor, processing temperature and processing time.

[0033] To avoid contact pad blistering based upon ethylene glycol/potassium hydroxide compositions, it is contemplated that the ratio of glycol to water should be in the range of from about 0.5:1 to about 8.5:1. It has been observed that pad blistering occurs when the ratio is less than about 0.5:1. The concentration of the hydroxide component, in particular potassium hydroxide, is dependent upon the ratio of glycol and water. By way of example, for 100 mls of glycol/water solution, the range of potassium hydroxide should be from about 40 to about 80 grams. The more water, the more potassium hydroxide is required to provide an effective color signal at the completion of the etching process.

[0034] As previously noted, the addition of glycol to the etchant composition increases the boiling point thereby enabling higher operating temperatures. It is contemplated that processing temperatures in the range of from about 180° to about 230°F will provide effective etching of the polyimide layer while minimizing pad blistering. If the process temperature is less than about 180°F, etching speed slows thereby requiring longer processing times. In accordance with the preferred embodiment, a processing temperature of about 180° to about 210°F is considered optimum. If the processing time becomes too long, significant undercutting of the contact pads around the via openings can occur. It has been observed that if etching is completed in about 6 to about 10 minutes, there is no evidence of pad blistering and undercutting is minimized. To assist in controlling of the etching speed, various inhibitors can be employed as previously described.

In accordance with one embodiment, K_3PO_4 and hexamethylene tetramine are preferred.

[0035] In accordance with another embodiment of the present invention, a two metal flexible substrate, i.e., 5 microns copper/50 microns polyimide/5 micron copper, was etched. The etchant composition was based upon a formulation including ethylene glycol present in the range of from about 50 to 100 ml, potassium hydroxide present in the range of from about 40 to about 80 grams, deionized water present in the range of from about 15 to about 50 ml, and hexamethylene tetramine in the range of from about 1 to 20 grams. The process of the present invention was carried out using the latter etchant composition including the steps as follows:

(1) Pre etch patterned copper foil at via sites to expose polyimide (both window and via in the case of certain single metal substrates).

(2) Plate gold or gold-copper-gold traces and leads on opposite side of the polyimide substrate (for two metal tape).

(3) Strip photoresist.

(4) Pretreatment: Dip substrate in hot DI water at about 160°F to about 180°F for 2 to 3 minutes.

(5) Dip substrate in the etching solution, at about 190° to about 210°F for 6 to 10 minutes, until red color covers the entire polyimide window.

(6) Post clean: Dip substrate in hot DI water at about 160°F to about 180°F for 3 to 5 minutes, until red color disappears.

(7) Spray rinse: DI water spray at room temperature for 2 minutes.

[0036] The etchant compositions of the present invention are particularly unique in that in addition to being an etchant, they can indicate completion of the etching of the polyimide substrate by appearance of a red color at the base

of the vias being etched. Chemical etchant compositions based upon dihydric alcohols and strong hydroxide bases, and preferably glycols and potassium hydroxide, provide an etchant composition and process which can be used to form micro-vias for interconnecting layers in microelectronic elements such as flexible circuit structures.

[0037] The etchant compositions of the present invention can be used for forming vias, bond windows and other openings in various microelectronic elements, such as two metal tape having plated through holes. By way of example, the etchant compositions of the present invention are suitable for making microelectronic elements as disclosed in Application No. 60/185,296 entitled "Single Image Process for Two-Sided Circuit" filed on February 28, 2000, the disclosure of which is incorporated herein by reference.

[0038] Referring to Figs. 4 and 5, the etchant compositions of the present invention can be used to manufacture a tented stencil 120 from a metal clad flexible sheet of polymer material, e.g., polyimide. As shown, the etching process using the etchant compositions of the present invention, as thus far described, forms a through hole 112. The opening in metal layer 104 is larger than the opening in metal layer 106 as a result of the etching process. The opening in metal layer 104 is large enough to receive a solder ball 114 so as to partially extend into the via. The opening in metal layer 106 can be used as a stencil mask for printing a material, such as flux or solder paste, onto the top surface of the solder ball 114. Material 116 may be simultaneously stencil applied to the top surfaces of a plurality of solder balls or solder bumps, by providing a stencil having a plurality of holes 112 which may be arranged in a corresponding matrix pattern. Although the solder balls or bumps may be attached to a common substrate or package during the stenciling operation, such attachment is not necessary. The plurality of

